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(54) Title: HEAT TREATMENT FOR NICKEL-BASE ALLOYS

(57) Abstract

A heat treatment for hot or cold worked 725 type corrosion resistant alloys to increase the room temperature yield strength of the material to above about 145 ksi (1000MPa). The material is useful for oil patch and gas turbine applications. The process includes annealing the material of about 825 °F (996 °C) for about 0.5–2.5 hours, age hardening the material at about 1700 °F (760 °C) for about 5.5 to 10.5 hours to precipate double gamma prime, furnace cooling the material about 50 °F (28 °C) to 100 °F (56 °C) per hour and heat treating the material at about 1200 °F (649 °C) for about 5.5 to about 12.5 hours.

HEAT TREATMENT FOR NICKEL-BASE ALLOYS

TECHNICAL FIELD

The instant invention relates to corrosion resistant nickel-base alloys in general, and more particularly, to a heat treatment that encourages gamma prime and double gamma prime precipitation and relatively high yield strengths on the order of 156-172 ksi (1076-1186MPa).

BACKGROUND ART

In physically and chemically demanding environments, such as oil patch and gas turbine applications, there is a need for higher strength nickel-base alloys having corrosion resistance greater than the workhorse 3% molybdenum precipitation hardened alloys – Inconel® alloy 718 and Incoloy® alloy 925. (Inconel and Incoloy are the trademarks of the assignee). In particular, a yield strength in the range of about 140-170 ksi (965-1172 MPa) combined with superior corrosion resistance is desired by fabricators and component manufacturers.

Oil patch applications include subsurface and well head completions and drill components. High strength and corrosion resistant containment rings and associated components on gas turbine engines require lightweight but robust construction.

Age hardenable alloys based upon nickel and containing precipitation hardening amounts of titanium, niobium and/or aluminum have been known and used for many years. Various heat treatment techniques have been employed to obtain desired physical and chemical characteristics. See, for example, U.S. patent 3,871,928.

More particularly, component fabricators and designers have identified the following characteristics and targets as desirable for specific oil/gas and turbine applications:

(1) Age-hardenable yield strengthen ≥ 140 ksi (968 MPa);

(2) Charpy V-notch impact strength at -75°F (-58°C) = 25 ft-lbs (111 N);

(3) Pitting resistance superior to alloys 718 (UNS NO 771B) and 925 (UNS NO 6625);

(4) Resistance to hydrogen embrittlement per NACE TM-0177 test;

(5) Stress corrosion cracking resistance to moderately sour oil field environments at temperatures from 250° to 350°F (121 to 177°C);

(6) Fracture energy as expressed by tensile strength elongation greater than exhibited by alloy 718; and

(7) High temperature strength greater than exhibited by alloy 625.

Assignee produces Inconel alloy 725 (UNS NO 7725). The typical commercial composition of alloy 725 is given below:

CHEMICAL COMPOSITION, WT. %	
Nickel	55.0-59.0
Chromium	19.0-22.5
Molybdenum	7.0-9.5
Niobium	2.75-4.0
Titanium	1.0-1.7
Aluminum	0.35 max.
Carbon	0.03 max.
Manganese	0.35 max.
Silicon	0.20 max.
Phosphorus	0.015 max.
Sulfur	0.010 max.
Commercial impurities	Trace
Iron	Remainder

Alloy 725 is strengthened by precipitation of double gamma prime phase during an aging treatment. Before aging, the alloy is currently solution annealed at 1900°F(1040°C) and water quenched. For sour gas applications, the published recommended aging treatment is 1350°F (730°C) / 8 hours and then air cooling.

In summary, in order to obtain the published high yield strengths for, say, age hardened rounds (133 ksi [917 MPa]) or strip (143 ksi [992 MPa]), the current practice is to anneal, cold work and then age.

In order to exceed the properties of alloys 718 and 925, it was contemplated that a new heat treatment paradigm would be necessary.

SUMMARY OF THE INVENTION

Accordingly, there is provided a heat treatment for 725 type alloys.

In contrast to current practice, the heat treatment is performed directly on hot or cold worked material.

The heat treatment consists of an initial anneal of about 1825°F (996°C) ± 25°F (14°C) for about 0.5 to 2.5 hours, followed by age hardening at about 1400°F (760°C) ± 50°F (28°C) for about 5.5 to 10.5 hours, followed by furnace cooling at about 50°F (28°C) ± 25°F (14°C) per hour to about 100°F (56°C) ± 25°F (14°C) per hour and finally heat treating the alloy at about 1200°F (649°C) ± 50° (28°C) for about 5.5 to 12.5 hours.

The resultant room temperature 0.2% yield strength of the alloy is in excess of about 145 ksi (1000 MPa), preferably above 150 ksi (1042 MPa); and more preferably in excess of 155 ksi (1069 MPa).

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 compares static crack growth data for alloy 725 and alloy 718 at 538°C (1000°F) in air.

Figure 2 compares static crack growth data for alloy 725 and alloy 718 at 649°C (1200°F).

PREFERRED EMBODIMENT OF THE INVENTION

For the purposes of this specification, the appearance of the adverb "about" before a single or series of values shall be interpreted to encompass each and every value unless expressly indicated to the contrary.

Although the inventors have endeavored to accurately convert units and measurements, in the event a discrepancy exists between an English unit of measurement and an SI unit of measurement, the English unit of measurement shall be controlling

The instant heat treatment process is applicable to 725 type alloys such as UNS designations NO 07725 and NO 07716.

Alloy UNS NO 07716 has the approximate ("about") analysis:

Nickel	61		
Molybdenum	8.5	Carbon	0.015
Niobium	3.3	Manganese	0.1
Titanium	1.3	Phosphorus	0.005
Aluminum	0.2	Sulfur	0.002
Iron	Remainder	Silicon	0.1
Commercial impurities	Trace	Chromium	20.5

The expression "725 type alloy" encompasses the approximate ranges of UNS NO 07725 and NO 07716. Accordingly for this specification, a "725 type alloy" may include the broad approximate lower and upper ranges of the identified component elements and/or the particular composition, identified in the UNS numbers and/or the particular examples disclosed herein.

In general, the alloy is initially annealed at about 1825°F (996°C) ± 25°F (14°C) for about 0.5 to 2.5 hours, followed by age hardening at about 1400°F (760°C) ± 50°F (28°C) for about 5.5 to 10.5 hours, followed by furnace cooling at about 50° F (90°C) ± 25°F (14°C) to about 100°F (180°C) ± 25°F (14°C) per hour and finally heat treating at about 1200° F (649°C) ± 50°F (28°C) for about 5.5 to 12.5 hours.

The resultant mechanical properties of an alloy 725 bar heat treated pursuant to the process disclosed herein are listed below:

0.2% Yield Strength ksi (MPa)	Tensile Strength ksi (MPa)	% Reduction of Area	% Elongation	Hardness HRC	-75° F (58° C) CVN Impact Strength ft-lb
156 - 172 (1076 - 1186 MPa)	195 - 216 (1345 - 1489 MPa)	35 - 46	21 - 25	38 - 42	27 - 42 (1120 - 187 N)

In contrast, the conventional existing treatment which calls for solution annealing plus age hardening optimizes corrosion resistance to extremely severe sour brine environments containing elemental sulfur at temperatures to 400° F (204°C). The specification yield strength is 120 ksi (827 MPa) minimum and 140 ksi (965 MPa) maximum.

Oil patch fabricators require higher strengths for flapper values in subsurface safety valves, packers and drilling equipment. Turbine manufactures require high fracture energies, as expressed by tensile strength times elongation, greater than those exhibited by alloy 718 and high temperature strengths greater than those exhibited by alloy 625.

The instant process does not solution anneal all the precipitates in the as hot worked structure which helps control grain size. The 1200°F (749°C) heat treating step grows the gamma double prime precipitates which are formed during the 1400°F (760°C) aging treatment. After the entire process is completed a higher yield strength is obtained. Acceptable ductility and toughness are maintained along with resistance to hydrogen embrittlement as per the NACE Test Method 0177 Oil Patch hydrogen embrittlement test.

The aforementioned test, promulgated by the National Association of Corrosion Engineers, is a severe hydrogen embrittlement test in which the material being tested is galvanically coupled to steel in an oil patch type sour brine environment consisting of hydrogen sulfide saturated 5% sodium chloride with 0.5% acetic acid at 77°F (25°C) for a minimum period of thirty days.

Without being limited to a particular theory, it is surmised that annealing the alloy at about 1825°F (996°C) partially dissolves the delta phase (Ni_3Nb) which is generally present in hot worked material (although the instant process is specifically applicable to cold worked forms as well). This helps tailor the microstructure by controlling the grain size. Further, the presence of the intergranular delta phase is also thought to improve the crack growth resistance at elevated temperatures under static or dynamic loading. The double aging treatment at 1400°F (760°C) and 1200°F (649°C) following annealing is designed to produce a morphology and volume fraction of Ni_3(Pl, Ti)-type gamma prime and Ni_3 (Nb, Al, Ti) - type double gamma prime precipitates to maximize the strength and ductility.

A number of tensile tests were conducted to evaluate the efficacy of the process.

PROCEDURE:

Material for testing came from commercially produced 1¼ in. to 2¼ inch (3.18-5.7 cm) diameter Inconel alloy 725 hot rolled bar. The chemical compositions of evaluated heats are shown in Table 1.

Table 1 Chemical Composition of Evaluated Heats (wt.%)

	HT5132LY	HT5143LY
C	0.005	0.005
Mn	0.07	0.13
Fe	8.46	8.05
S	0.002	0.003
Si	<0.01	0.02
Cu	0.01	0.01
Ni*	57.64	57.82
Cr	20.73	20.81
Al	0.11	0.16
Ti	1.55	1.5
Co	<0.01	0.03
Mo	7.92	7.95
Nb	3.48	3.53
P	0.004	0.004
B	0.003	0.003

*Balance element, approximate composition.

A hydrogen embrittlement test was conducted in accordance with the aforementioned NACE Test Method TM-0177 (A). Specimens were galvanically coupled to steel. A minimum test duration of 720 hours is required by the specification. In this case, the heat treated Inconel alloy 725 specimens were removed from the environment after 725 hours of exposure.

DATA REVIEW:

Table 2 displays the mechanical properties for alloy 725 hot rolled bar, evaluated in various heat treated conditions. Except for heat treatments 5 and 6, the remaining heat treatments fall within the inventive concept. Material in these heat treated conditions exhibited excellent strength, ductility and toughness.

Table 2 Mechanical Properties alloy 725, Hot Rolled Bar

Heat	Heat Treatment	Room Temperature Tensile				HRC	-75°F CVN (-58°C) Impact Strength (N)	Lateral Expansion in (mm)
		YS ksi (MPa)	ULT ksi (MPa)	%RA	%EL			
HT5132LY(22)	1	168.6 (1162)	212.3 (1464)	40.8	22.5	42		
	2	170.6 (1176)	213.2 (1470)	40.4	22.6	40		
	3	167.0 (1151)	211.4 (1458)	39.9	21.9	41		
HT5132LY(24)	4	172.1 (1187)	215.8 (1488)	35.6	20.6	42		
HT5143Y(31)	5	145.3 (1002)	203.5 (1403)	35.1	22.9	39		
	6	140.5 (969)	201.4 (1389)	35.0	23.7	36		
HT51432Y(13)	1	158.1 (1090)	198.9 (1371)	43.3	25.2	39	(129) 29;30(133)	(0.33) 0.013;0.020 (0.51)
	2	160.1 (1104)	202.3 (1395)	45.7	25.4	41	(165) 37;37 (165)	0.41) 0.016;0.019 (0.48)
	3	150.6 (1038)	193.2 (1322)	44.4	24.6	39	(116) 26;26 (116)	(0.36) 0.014;0.012 (0.30)
	4	158.3 (1091)	198.5 (1369)	40.7	25.1	38	(120) 27;29 (129)	(0.36) 0.014;0.017 (0.43)
	5	137.7 (949)	193.4 (1333)	39.7	25.5	38	(98) 22;20 (89)	(0.43) 0.017;0.012 (0.30)
	6	133.0 (917)	190.4 (1313)	38.3	25.8	34	(107) 24;23 (102)	(0.30) 0.012;0.013 (0.33)
	7	158.5 (1093)	197.1 (1359)	43.8	24.7	40	(116) 26;26 (116)	(0.36) 0.014;0.013 (0.33)
	8	158.5 (1093)	199.1 (1373)	44.0	24.6	38	(178) 40;32 (142)	(0.53) 0.021;0.048 (1.22)
	9	156.2 (1077)	197.5 (1362)	42.7	25.1	39	(133) 30;33 (147)	(0.41) 0.016;0.010 (0.25)
	10	157.7 (1087)	195.0 (1344)	42.2	24.8	41	(173) 39;42 (187)	(0.43) 0.017;0.017 (0.43)

Heat Treated Condition:

1: 1825°F (996°C)/1h/AC + 1400°F(760°C)/10h,FC at 50°(90°C)/h to 1200°F(649°C)/8h/AC
2: 1825°F (996°C)/1h/AC + 1400°F(760°C)/6h,FC at 50°(90°C)/h to 1200°F(649°C)/12h/AC
3: 1825°F (996°C)/1h/AC + 1400°F(760°C)/14h,FC at 50°(90°C)/h to 1200°F(649°C)/4h/AC
4: 1825°F (996°C)/1h/AC + 1400°F(760°C)/10h,FC at 50°(90°C)/h to 1200°F(649°C)/8h/AC
5: 1825°F (996°C)/1h/AC + 1550°F(843°C)/3h,AC + 1400°F/8h, FC at 50°/h to 1150°F (621°C) /8h/AC
6: 1850°F (1010°C)/1h/AC + 1400°F(760°C)/3h,FC at 50°(90°C)/h to 1200°F(649°C)/8h/AC
7: 1825°F (996°C)/2h/AC + 1400°F(760°C)/6h,FC at 50°(90°C)/h to 1200°F(649°C)/8h/AC
8: 1825°F (996°C)/2h/AC + 1400°F(760°C)/6h,FC at 50°(90°C)/h to 1200°F(649°C)/6h/AC
9: 1825°F (996°C)/2h/AC + 1400°F(760°C)/6h,FC at 50°(90°C)/h to 1200°F(649°C)/12h/AC
10: 1825°F (996°C)/1h/AC + 1400°F(760°C)/6h,FC at 50°(90°C)/h to 1200°F(649°C)/6/AC
(FC = Furnace Cool, AC = Air Cooling h=hour)
(VN = Charpy - V-Notch, HRC = Hardness Rockwell C.RA = Reduction in Area, EL = Elongation))

Samples 4, 8, 9 and 10 were subjected to and passed the NACE Test Method 0177 (A) oil patch hydrogen embrittlement test. After 725 hours of exposure to the sour brine environment, there was no cracking f duplicate specimens coupled to steel. Results are shown in Table 3.

Table 3. TM0177 (A) Hydrogen Embrittlement Test* Results

Heat Treated Condition	Test Duration, hours	Comment
4	725	Passed, no cracking
8	725	Passed, no cracking
9	725	Passed, no cracking
10	725	Passed, no cracking
*Tested galvanically coupled to steel		

An additional series of experimental heat treatment tests were undertaken on a forged ring made from alloy 725.

A 6 inch (15.2 cm) diameter forging stock round of heat HT6094L Y (alloy 725) was forged to a ring (13 inch [33cm] outer diameter, 8 inch [20.3 cm] inner diameter, and 3 inch [7.6 cm] height). The chemical composition of heat HT6094L Y is given in Table 4.

Table 4. Chemical Composition of Heat HT6094L Y.

Ni	Cr	Fe	Mo	Nb	Ti	Al	C
58.08	20.73	7.71	7.99	3.47	1.52	0.21	0.010

The forged ring was subjected to annealing at 1800°F (982°C), 1825°F (996°C), and 1850°F (1010°C) for one hour. These annealing conditions provided fully recrystalized microstructure with grain sizes of ASTM #7, 6, and 5 respectively. The material annealed at 1825°F (996°C) was subjected to three aging conditions coded A, B, and C. The aging conditions are given below:

A= 1325°F (718°C)/8h, Furnace Cool at 100°F (56°C)/h to 1150°F (621°C), Hold at 1150°F(621°C)/8h, Air Cool

B= 1400°F(760°C)/10h, Furnace Cool at 100°F(56°C)/h to 1200°F(649°C), Hold at 1200°F(649°C)/8h, Air Cool

C= 1550°F(843°C)/3h Air Cool + 1325°F (718°C)/8h, Furnace Cool at 100°F(56°C)/h to 1150°F(625°C), Hold at 1150°F(625°C)/8h, Air Cool

Code B's heat treatment resulted in the best combination of properties for room temperature tensile, 1200°F (649°C) tensile, and 1200°F-110ksi [649°C-758 MPa] stress rupture (Tables 5, 6 and 7). Therefore, code B heat treatment was selected to evaluate long term stability and crack growth resistance. The tensile properties reported are the averages of duplicate tests.

Table 5. Room Temperature Tensile Properties.

Heat Treatment	Yield Strength ksi (MPa)	Tensile Strength ksi (MPa)	% Elongation	Reduction of Area
A	132 (910)	190 (1310)	27	53
B	150 (1034)	198 (1365)	21	41
C	141 (972)	195 (1344)	21	36

Table 6. High Temperature (1200°F) Tense Properties

Heat Treatment	Yield Strength ksi (MPa)	Tensile Strength ksi (MPa)	% Elongation	Reduction of Area
A	111 (765)	160 (1103)	36	59
B	127 (876)	171 (1179)	27	43
C	120 (827	168 (1158)	31	54

Table 7. Combination Bar Stress Rupture Tests at 1200°F-110ksi.

Heat Treatment	Rupture Life, h	% Elongation	Reduction in Area
A	35.6	14.7	29.8
	53.3	24	22.2
B	45.2	43.5	49
	31.8	23.6	29.2
C	11.8	40.8	52
	12.4	28.6	32.9

Table 8 shows room temperature tensile properties of the material exposed at 1100°F (593°C) up to 5000h. The initial 500h exposure increased the room temperature

yield strength to 160ksi (1103MPa) and thereafter it remained constant up to a total exposure time of 5000h. Room temperature elongation and reduction of area did not change with exposure. The initial 500h exposure at 1100°F (593°C) increased the 1200°F (649°C) yield strength to 134ksi (924MPa) (Table 9) and thereafter it remained constant up a total exposure time of 7500h. High temperature elongation essentially remained constant with exposure except 1000h exposure with had low elongation of 16%.

Table 8. Room Temperature Tensile Properties of As-produced (Code B heat treated) and 1100°F (593°C) Exposed Material.

Exposure Condition	Yield Strength ksi (MPa)	Tensile Strength ksi (MPa)	% Elongation	Reduction of Area
As-produced	150 (1034)	198 (1365)	21	41
500 hours	161 (1110)	205 (1413)	20	44
1000 hours	158 (1089)	202 (1993)	21	44
5000 hours	159 (1096)	203 (1399)	18	34

Table 9. High Temperature (1200°F [649°C]) Tensile Properties of As-produced (Code B heat treated) and 1100°F (598°C) Exposed Material.

Exposure Condition	Yield Strength ksi (MPa)	Tensile Strength ksi (MPa)	% Elongation	Reduction of Area
As-produced	127 (876)	171 (1179)	27	43
500 hours	134 (924)	175 (931)	29	50
1000 hours	134 (924)	176 (1213)	16	23
2500 hours	133 (917)	176 (931)	24	39
7500 hours	134 (924)	176 (1213)	27	44

Figures 1 and 2 compare the crack growth data of alloys 725 and 718 at 1000°F (538°C) and 1200°F (649°C) in air. Crack growth resistance of alloy 725 when processed in accordance with the instant heat treatment is at least an order of magnitude better than standard treated alloy 718.

In summary, the heat treatment of annealing the worked alloy at about 1825°F (996°C)/10h air cooling + about 1400°F (760°C)/10h, furnace cooling at about 100°F (56°C)/h to 1200°F (649°C), holding at about 1200°F (649°C)/8h, and air cooling provided the best combination of properties for room temperature tensile, high temperature tensile, and stress rupture. The material subjected to this heat treatment demonstrated

excellent long term thermal stability at 1100°F (593°C). Further, the static crack growth resistance of alloy 725 subjected to this heat treatment was at least an order of magnitude better than alloy 718 at 1000°F(538°C) and 1200°F(649°C).

In accordance with the provisions of the statute, the specification illustrates and describes specific embodiments of the invention. Those skilled in the art will understand that changes may be made in the form of the invention covered by the claims; and that certain features of the invention may sometimes be used to advantage without a corresponding use of the other features.

The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:

1. A process for heat treating an age hardenable 725 type alloy nickel-base alloy to a yield strength in excess of about 145 ksi (100MPa) the method comprising:

a) providing a hot or cold worked material consisting essentially of 725 type alloy;
b) annealing the material at about 1825°F (996°C) ± 25°F (14°C) for about 0.5 to 2.5 hours;
c) age hardening the material at about 1400°F (760°C) ± 50°F (28°C) for about 5.5 to 10.5 hours;
d) furnace cooling the material to about 1200°F (649°C); and
e) heat treating the material at about 1200°F (649°C) ± 50°F (28°C) for about 5.5 to 12.5 hours.

2. The process according to claim 1 including furnace cooling the material about 50°F (28°C) ± 25°F (14°C) per hour to about 100°F (56°C) ± 25°F (14°C) per hour.

3. The process according to claim 1 comprising:
a) annealing the material at about 1825°F (996°C) for about 10 hours;
b) age hardening the material at about 1400°F (760°C) for about 10 hours;
c) furnace cooling the material at about 100°F (56°C) per hour to about 1200°F (649°C), and
d) heat treating the material at about 1200°F (649°C) for about 8 hours.

4. The process according to claim 1 wherein the 725 type alloy is selected from the group consisting of UNS NO 07725 and UNS NO 07716.

5. The process according to claim 1 including forming gamma double prime particles in the 725 type alloy during age hardening.

6. The process according to claim 1 wherein the room temperature yield strength of the material is about 156-172 ksi (1076-1186 MPa).

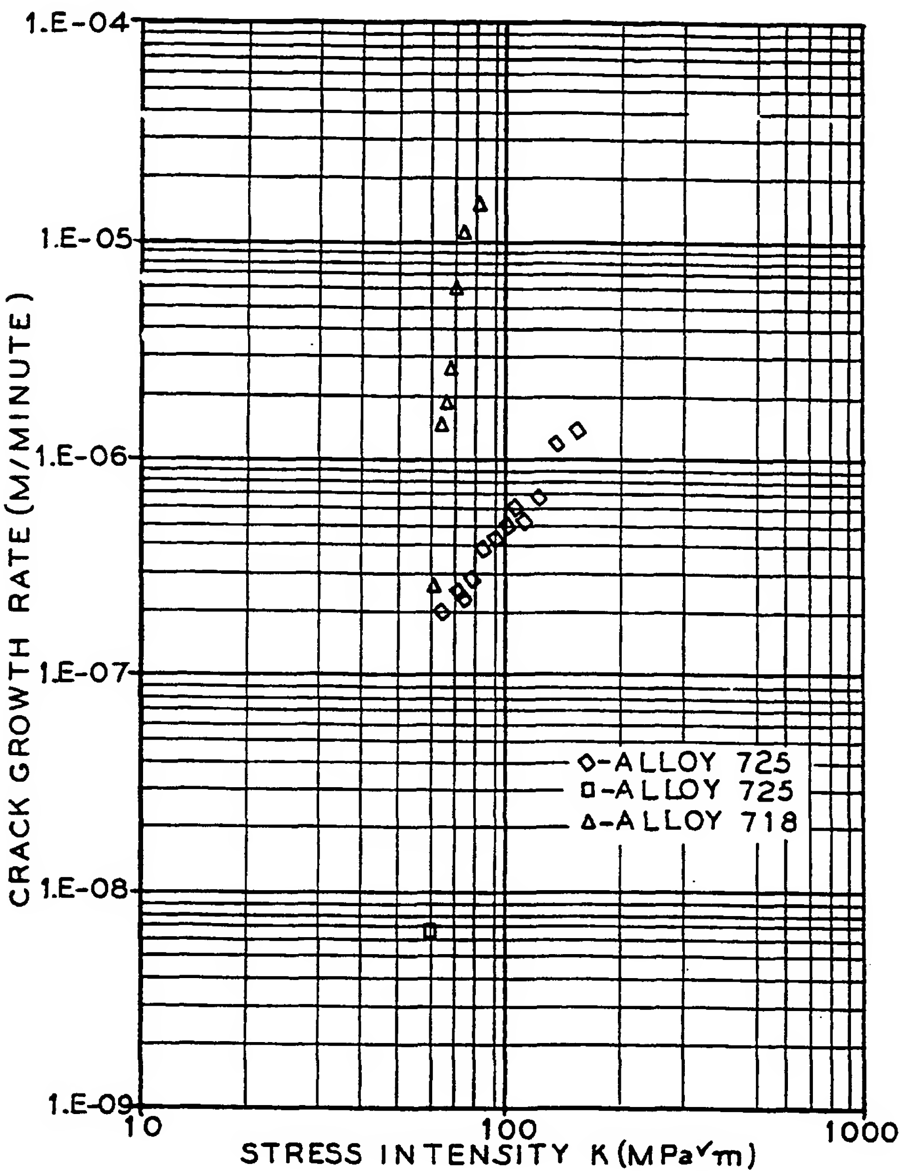
7. The process according to claim 1 wherein the 725 type alloy consists essentially of about 55-59% nickel, about 19-22.5% chromium, about 7-9.5% molybdenum, about 2.75-4% niobium, about 1-1.7% titanium, up to about 0.35% aluminum, up to about 0.03% carbon, up to about 0.35% manganese, up to about 0.2% silicon, up to about 0.015% phosphorus, up to about 0.01% sulfur commercial impurities and balance iron.

8. The process according to claim 1 wherein the 725 type alloy consists essentially of about 61% nickel, about 20.5% chromium, about 8.5% molybdenum, about 1.3% titanium, about 3.3% niobium, about 0.2% aluminum, about 0.015 carbon, about 0.1% manganese, about 0.1% silicon, about 0.005% phosphorus about 0.002% sulfur, commercial impurities and balance iron.

9. The process according to claim 1 wherein the 725 type alloy consists essentially of about 55-61% nickel, about 19-22.5% chromium, about 7-9.5% molybdenum, about 2.75-4% niobium, about 1-1.7% titanium, up to about 0.35% aluminum, up to about 0.03% carbon, up to about 0.35% manganese, up to about 0.2% silicon, up to about 0.015% phosphorus, up to about 0.01% sulfur commercial impurities and balance iron.

10. The process according to claim 1 wherein the 725 type alloy has a Charpy-V-notch impact strength equal to or greater than about 25 ft-lbs (111N).

FIG. 1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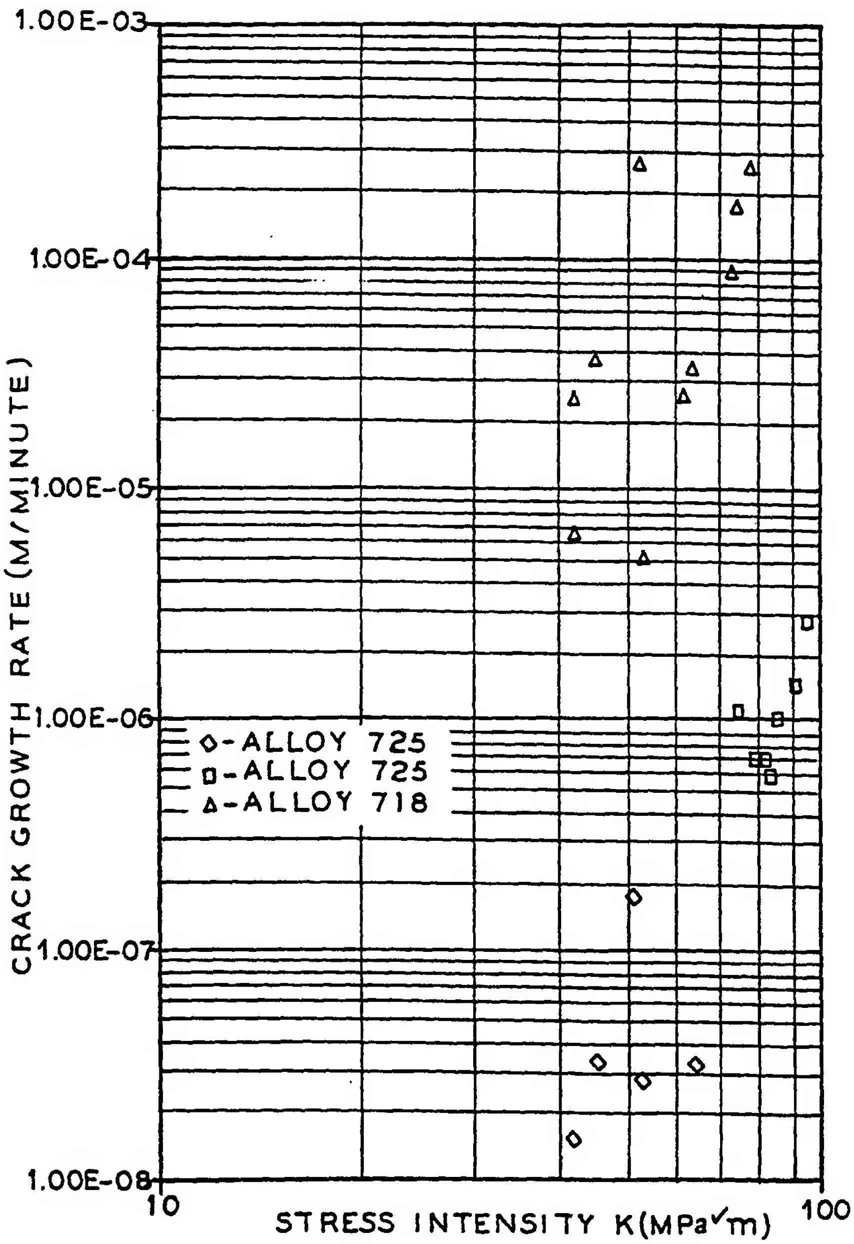
□-ALLOY 725
△-ALLOY 718

FIG.2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◇-ALLOY 725
□-ALLOY 725
△-ALLOY 718
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100
STRESS INTENSITY K(MPa√m)

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US99/14000

A. CLASSIFICATION OF SUBJECT MATTER
IPC(6) :C22F 1/10
US CL :148/675, 676, 677
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
U.S. : 148/675, 676, 677

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
NONE

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
APS-USPAT, Ni, Cr, Mo, anneal?, aging, age harden?, cool?

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 5,556,594 A (FRANK et al.) 17 September 1996, column 8, line 60 - column 9, line 18.	1-10
A	US 5,244,515 A (MIGLIN) 14 September 1993, column 3, Tables 1-3.	1-10
A	US 5,059,257 A (WANNER et al.) 22 October 1991, column 4, Table 1; column 6, lines 49-65; and column 8, lines 45-68.	1-10
Y	US 4,979,995 A (HATTORI et al.) 25 December 1990, column 2, lines 20-27; column 4, line 64 - column 5, line 29.	1-10

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

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Date of the actual completion of the international search	Date of mailing of the international search report
28 OCTOBER 1999	04 NOV 1999

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